

Impact of fertiliser nitrogen formulation, and N stabilisers on nitrous oxide emissions in spring barley

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Roche, L., Forrestal, P. J., Lanigan, G. J., Richards, K. G., Shaw, L. J. and Wall, D. P. (2016) Impact of fertiliser nitrogen formulation, and N stabilisers on nitrous oxide emissions in spring barley. *Agriculture, Ecosystems and Environment*, 233. pp. 229-237. ISSN 0167-8809 doi: 10.1016/j.agee.2016.08.031 Available at <https://centaur.reading.ac.uk/66747/>

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To link to this article DOI: <http://dx.doi.org/10.1016/j.agee.2016.08.031>

Publisher: Elsevier

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Title: Impact of fertiliser nitrogen formulation, and N stabilisers on nitrous oxide emissions in spring barley

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Abstract

The application of nitrogen (N) fertilisers to agricultural soils is a major source of nitrous oxide (N₂O) emissions. The Intergovernmental Panel on Climate Change (IPCC) has set a default emission factor of 1% (EF₁) for N fertiliser applied to managed agricultural soils. This value does not differentiate between different N fertiliser formulations or rates of N application. The objective of this field study under spring barley was to determine N₂O EF's for different N fertiliser formulations including urea and urea stabilised with the nitrification inhibitor dicyandiamide (DCD) and/or the urease inhibitor *N*-(*n*-butyl) thiophosphoric triamide (NBPT) and to evaluate their N₂O loss abatement potential relative to calcium ammonium nitrate (CAN). The highest EF₁ measured was 0.49% for CAN which was less than half the IPCC default value of 1%. While the urease inhibitor did not reduce emissions relative to CAN; the nitrification inhibitor significantly reduced emissions compared to CAN with EF₁ as low as 0.00% for a typical spring barley site. There was no significant impact of CAN or urea application rate on EF₁ but there was a significant negative relationship

27 observed for urea in 2013. The study highlights the importance of generating higher Tier
28 emission factors in terms of fertiliser type for use in national inventories.

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30 **Keywords:** urea; emission factor; arable soil; DCD; Inhibitors; NBPT

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1 Introduction

Concentrations of atmospheric greenhouse gases (GHGs) have increased since the beginning of the industrial era, due to anthropogenic activities (U.S. EPA, 2015). Between 1990 and 2005, global non-carbon dioxide (CO₂) GHG emissions grew by 10% to approximately 10,800 megatons CO₂ equivalent (Mt CO₂ eq) and are expected to increase by 43% by 2030 (U.S. EPA, 2012). Globally, the agriculture sector accounts for the largest proportion of non-CO₂ GHG emissions, accounting for 54% in 2005 (U.S. EPA, 2012). Nitrous oxide comprises approximately 32% of agricultural emissions (U.S. EPA, 2012) and is a potent GHG, with a global warming potential 265 times that of CO₂ over a 100 year time frame (Myhre et al., 2013). The atmospheric concentration of N₂O has increased at an average rate of 0.75 ppb yr⁻¹, rising 20% since 1750 to 324 ppb (IPCC, 2014). Emissions associated with nitrogen (N) application to agricultural soils comprise 60% of global N₂O emissions and are projected to increase from 6.1 to over 7 Tg N₂O-N yr⁻¹ by 2030, due to increased global population and food demand (Reay et al., 2012). The use of mineral fertilisers has been one of the principal drivers of this increase in emissions (Davidson, 2009). Excess N application has resulted in enhanced reactive N losses to the environment (Bell et al., 2015). Furthermore N₂O is the single most important ozone-depleting gas and is expected to remain so throughout the 21st century (Ravishankara et al., 2009).

In order to generate total N₂O emissions for inputting into national inventories, the quantity of a given activity (e.g. tonnes of fertiliser applied) is multiplied by an emission factor (EF). This emission factor is defined as the percentage of N₂O emitted as a proportion of the N applied. The IPCC default EF for direct N₂O emissions, associated with the application of mineral or organic fertiliser to managed soils, (termed EF₁) is 1% of the N applied (IPCC, 2006). This value is a crude estimate as it does not account for crop and soil type, climatic conditions or management practices, all of which affect N₂O emissions (Dobbie and Smith,

2003a, 2003b; Dobbie et al., 1999; Lesschen et al., 2011). Country and cropping system specific data would allow temperate regions to use the Tier 2 emission inventory methodology, where these more detailed and accurate emission factors that are specific for soil and crop type are required (IPCC, 2006). Subsequently, these data could support the development of new N fertiliser recommendations in Ireland; therefore promoting continued reductions of GHG emissions in line with the 2030 targets to reduce GHG emissions by 40% (EC, 2014).

In Ireland the agricultural sector contributes 32% of national GHG emissions (Duffy et al., 2015). Nitrogen application to agricultural soils is one of the key categories, accounting for 22% of total emissions from agriculture and this is projected to increase by 12% by 2020 (EPA, 2013). The focus of this study is on arable land, specifically examining the N₂O emissions resulting from the addition of N fertiliser to spring cereal crops, which is one of the largest contributors to GHGs from this land use type. Altering fertiliser formulation and/or rate as well as the incorporation of inhibitors may be a key abatement strategy for reducing N₂O emissions from agriculture (Harty et al., 2016).

Calcium ammonium nitrate (CAN) is the dominant N fertiliser used by arable farmers in Ireland. CAN contains 27% N, of which 50% is in the nitrate-N form and immediately contributes to the soil nitrate pool. Nitrate is then available for N₂O loss through the denitrification processes. Nitrification may also be an important source of N₂O from the application of urea or ammonium based fertilisers (Bremner and Blackmer, 1978). Substituting CAN with urea as an alternative N fertiliser formulation has the potential to reduce direct N₂O emissions, associated with denitrification, because urea or ammonium N forms are not immediately available for denitrification after application. However, there is potential for nitrifier denitrification to be a source of N₂O (Kool et al., 2011) coupled with the potential for urea to favour N loss as ammonia during urea hydrolysis. The addition of a

urease inhibitor has potential to reduce ammonia volatilisation which not only contributes to air pollution but which can also contribute to indirect N₂O emissions (Watson et al., 2009; Forrestal et al., 2015). The addition of a nitrification inhibitor has potential to regulate the soil nitrate pool and further reduce direct N₂O emissions by both nitrification and denitrification (Dobbie and Smith, 2003a). The rate of N fertiliser application is also important as generally the higher the N fertiliser rate, the higher the N₂O emissions (Hinton et al., 2015). Using the IPCC default EF₁ assumes a linear relationship between N₂O emissions and N fertiliser rate which Hinton et al (2015) observed. Other studies have observed nonlinear relationships between N₂O emissions and N fertiliser rate (Hoben et al., 2011; McSwiney and Roberston, 2005).

In this study, N₂O emissions were measured from spring barley after fertiliser applications of CAN and urea with and without N stabilisers. Nitrogen stabilisers are fertiliser additives that reduce environmental N losses thereby stabilising the N in the soil. These can either a) reduce urea N loss via volatilisation and are termed urease inhibitors or reduce N loss via denitrification of nitrate and are termed nitrification inhibitors. These stabilisers can thus increase fertiliser use efficiencies by increasing plant N uptake and crop yields. The N stabilisers evaluated in this study were the urease inhibitor N-(n-butyl) thiophosphoric triamide (NBPT (trade name Agrotain™) and also referred to as n-BTPT in other studies), the nitrification inhibitor dicyandiamide (DCD), and the Maleic-Itaconic acid Co-polymer (MICO (trade name NutriSphere-N®)) which is a urease and nitrification inhibitor. The aims of this study were to quantify the effect of N fertiliser rate and formulation on direct N₂O emissions from spring barley in a temperate maritime climate and to develop crop specific emission factors for use in national N₂O emissions inventories. The hypothesis of this study is that changing N fertiliser source from CAN to stabilised urea reduces N₂O emissions.

2 Materials and Methods

2.1 Site description

Field plot trials were conducted on spring malting barley on a free-draining loam soil located in Marshalstown, Co. Wexford (Table 1). This field site was located within the main malting barley growing region in Ireland (Duffy et al., 2015) and was representative of the typical soil type used for arable cropping. The site history was long term arable production for at least 20 years.

2.2 Crop husbandry

The spring barley (*Hordeum vulgare* L.) cultivar used was ‘Sebastian’. The site was ploughed to approximately 20 cm depth in February 2013 and March 2014. The crop was sown in mid-April in both years and was harvested in mid-August in both years. The experiment ran from April 2013 to April 2015 and generated emission factors for two years (crop sowing time to the following sowing time each year). The site characteristics are described in Table 1 and are based on the top 10 cm of soil which is the standard agronomic soil sampling depth in Ireland. Each year basal P, K and S were applied to the soil, according to the Teagasc Green Book of nutrient advice (Coulter and Lalor, 2008) to prevent nutrient deficiencies from occurring. A robust pesticide programme was applied to the crop to control weeds, pests and diseases as per standard agronomic practice for spring barley crops (Teagasc, 2015).

132 **Table 1.** Site location and soil characteristics (0-10 cm depth)

GPS Co-ordinates	52° 33' 37.3" N 6° 36' 09.0" W
Drainage Class	Free- draining
Texture	Loam
Sand %	31.8
Silt %	41.4
Clay %	26.8
Stone volume (v/v)	28
pH	6.76
LOI %	8.99
Total C %	2.88
Total N %	0.281
C : N ratio	10
CEC (meq/100g)	21.1
Ca (mg/kg soil)	1616
K (mg/kg soil)	267
Mg (mg/kg soil)	164
P (mg/kg soil)	37.3
S (mg/kg soil)	4.8

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135 2.3 Experimental Design

136 A randomised block design was used with five replicates of each fertiliser formulation. In
 137 addition to the unfertilised control, six fertiliser formulations were used: (i) CAN, (ii) urea
 138 (iii) urea + NBPT (iv) urea + DCD (v) urea + NBPT + DCD, and (vi) urea + MICO included
 139 in 2014 only. All fertiliser formulations were applied at the common N rate of 150 kg N ha⁻¹

as this was the recommended N rate for spring barley as per the target crop yield. CAN and urea were applied at additional rates and details of the N fertiliser rates used are shown in Table 2. Each experimental unit (trial plot) measured 6m by 2.5m. Fertiliser was applied in two splits for all treatments. The first split comprised 30 kg N ha⁻¹ and was surface applied within seven days of sowing. The second split was comprised of the remaining N fertiliser to make up the individual treatment rate (for 150 kg N ha⁻¹ the 2nd split was 120 kg N ha⁻¹) and was applied during early to mid-tillering (Zadoks GS 20-25). The first split fertiliser was applied 15th April 2013 and the 23rd April 2014. The second split was applied 13th May in both years. Pre-weighed fertiliser was applied by hand to the chamber base separately to the plot area to ensure the correct N application rate within the chambers.

Table 2. Nitrogen fertiliser formulations and rate

Fertiliser Formulation	N Rate (kg N ha ⁻¹)				
	100	125	150	175	200
CAN	✓	✓	✓	✓	✓
Urea	✓	✓	✓		✓
Urea + NBPT			✓		
Urea + DCD			✓		
Urea + NBPT + DCD			✓		
Urea + MICO			✓		

2.4 Soil and Climatic Analysis

Total daily rainfall, air temperature and humidity were recorded at a weather station adjacent to the site. Atmospheric pressure from the nearest available weather station at Johnstown Castle was used. Soil moisture was recorded on each day of N₂O measurement to a depth of

10 cm using a Delta T ML2 probe (Delta-T Devices, Burwell, Cambridge, UK). In addition to this, soil samples were taken on a weekly basis at the beginning of the year and on each day of measurement once the frequency of N₂O measurement was reduced later in the growing season. The gravimetric water content (GWC) of the soil was measured using these soil samples. Soil samples were taken to 10 cm depth using a soil corer (2 cm diameter). Five cores were taken from each plot, bulked together in sealed plastic bags and placed in a cool-box. Following sampling (i.e. within 2 hours) the soil samples were taken to the laboratory where they were wet sieved to 2 mm followed immediately by mineral N extraction using 2M potassium chloride (KCl) (1:5 ratio of soil to KCl) (Keeney and Nelson, 1982; Mulvaney, 1996). The mineral N extracts were analysed colorimetrically using an Aquakem 600A (Aquakem 600A, 01621, Vantaa, Finland) to determine the concentration of the mineral N species i.e. Total Oxidised N (TON (including nitrite (NO₂⁻) and nitrate (NO₃⁻)) and ammonium-N (NH₄⁺-N). Soil sampling and mineral N extraction occurred weekly at the beginning of the experiment and was reduced to once fortnightly coinciding with the frequency of N₂O measurements. The gravimetric water content (GWC) of the soil samples was also measured on each day of sampling. Soil bulk density was measured four times over the course of the experiment (after the crop was planted and after harvest) and this was used with GWC to calculate volumetric water content (VWC). Soil bulk density and VWC were used to calculate water filled pore space percentage (WFPS %)

2.5 Nitrous oxide (N₂O) sampling and analysis

Daily N₂O fluxes were measured using the static chamber technique (Smith et al., 1995; Chadwick et al., 2014), adhering to the methodology guidelines compiled by the Global Research Alliance (de Klein and Harvey, 2012). The N₂O chamber measurement area was 0.4m². Collars were installed to at least 5 cm into the soil (Smith et al., 2012) and contained a

183 neoprene filled channel in order to maintain an air-tight seal. Collars were installed at least
184 three days prior to the first sampling and were left in place for the duration of the study.
185 Collars were removed for harvest and ploughing events and then reinstalled afterwards.
186 When sampling, a stainless steel lid was placed onto the collar and a 10 kg weight was placed
187 on top to compress the neoprene gasket, thus ensuring an airtight seal inside the chamber.
188 There were two different chamber sizes. A chamber with air volume 0.017 m^3 (10cm height)
189 was used from sowing until Zadoks GS 32-33 (stem extension). Subsequently, larger
190 chambers with an air volume of 0.096 m^3 (60cm height) were used until harvest, after which
191 small chambers were used again. Chambers were sampled prior to fertilisation, and then on a
192 reducing temporal resolution for four weeks after fertiliser was applied i.e. four times per
193 week for the first two weeks, twice per week for the next two weeks, and once per week
194 thereafter. This sampling frequency was adopted to capture the period of most active N loss
195 in more detail. In Year two, N_2O sampling was reduced to once every three weeks (after the
196 initial four weeks of sampling after fertilisation) after reviewing year one data. The chamber
197 lids were left on for 40 minutes, (larger chamber lids were left on for 60 minutes), then a 10
198 ml sample was taken from each chamber and immediately injected into a 7 ml pre-evacuated
199 exetainer (Sigma-Aldrich, UK) fitted with double wadded septa (Labco, High Wycombe,
200 UK). On each sampling date eight samples of ambient air were taken around the site and the
201 average used as time zero (T_0) sample for each chamber. Chadwick et al. (2014) have shown
202 that ambient samples are a useful surrogate for individual chamber T_0 samples. On each
203 sampling day, five chambers were chosen at random to check for linearity. These chambers
204 were sampled at T_0 , T_{15} , T_{30} , T_{40} , T_{60} and samples were statistically analysed to test for
205 flux/no flux, quadratic or linearity. On each sampling day two sampling vials were injected
206 with 0.5 ppm N_2O standard from the laboratory to ensure the integrity of samples during
207 storage. Samples were analysed for N_2O using an electron capture detector (ECD) at 300°C .

A CTC Analytics Combi-pal auto sampler (CTC Analytics, Industriestrasse 20, Zwingen, Switzerland) was used to inject gas samples into the Bruker Gas Chromatograph (Bruker, Bremen, Germany). Evolved N₂O was expressed as parts per million by volume (ppmv) having allowed for ambient concentrations and up-scaled to a flux in g N₂O-N ha⁻¹ d⁻¹ using the following equation adapted from de Klein and Harvey (2012):

$$F_{N_2O} = (\partial c / \partial t) * ((M * P) / R * T) * (V / A)$$

Where:

∂c is the change in gas concentration in the chamber headspace during the enclosure period (ppbv), ∂t is the enclosure period expressed in minutes, M is the molar mass of N₂O-N (28 g mol⁻¹), P is atmospheric pressure (Pa) at the time of sampling, T is the temperature (K) at the time of sampling, R is the ideal gas constant (8.314 J k⁻¹ mol⁻¹), V is the headspace volume of the chamber and A is the area covered by the chamber (ha).

Sampling occurred between 10 am and 2 pm each day as per Chadwick et al. (2014). The limit of detection of the method was calculated by averaging the standard deviation of all ambient samples for each year and then subtracting three standard deviations. This was 0.26 ppm and 0.28 ppm for 2013 and 2014, respectively. Anything below this was excluded from the study. In total over the two years 39 data points were removed as limits of detection out of a total of 5980 data points.

2.6 Emission Factor calculation

Cumulative N₂O fluxes from each chamber were calculated using trapezoidal integration to interpolate fluxes between sampling dates. Trapezoidal integration was used to linearly integrate fluxes from one sampling day to the next sampling day in order to generate fluxes for 365 days in order to generate cumulative fluxes. For each formulation, cumulative fluxes

were calculated using the mean of the five replicates. The EFs were then calculated using the following equation:

$$EF (\%) = \frac{N_2O-N \text{ cumulative (formulation)} - N_2O-N \text{ cumulative (unfertilised control)}}{Fertiliser N \text{ applied}} \times 100$$

Annual EFs were calculated over a 365 day period (IPCC, 2006). As calendar year (January – December) measurement is not appropriate for tillage systems, EFs were calculated from sowing date to the subsequent years sowing date and normalised to 365 days. Nitrous oxide yield efficiency was calculated by dividing the cumulative $N_2O-N \text{ ha}^{-1}$ (kg) of a treatment by the grain yield (t ha^{-1}) for the same treatment which produced N_2O yield efficiency ($\text{kg } N_2O-N \text{ t}^{-1} \text{ grain}$).

2.7 Linearity of N_2O flux

Results from the randomly selected N_2O chambers, used to assess if the N_2O flux was linear, showed on average linear accumulation. Initial analysis of this data was conducted to assess if a flux in N_2O emissions occurred. In some cases there was no flux evident (Table 3). The chambers showing N_2O flux were then analysed for linear or quadratic accumulation of N_2O . Over 90% of these chamber measurements in both sites in both years showed linear accumulation according to the criteria of Chadwick et al. (2014) (Table 3). This shows that the assumption of linear accumulation in the headspace can be used. This is in agreement with work conducted by Chadwick et al. (2014) where over 90% of chamber measurements ($n=1970$) from multiple field experiments, showed linear N_2O accumulation.

258 **Table 3.** Linearity samples for 2013 and 2014

	2013	2014
Total No. chambers	260	212
Chambers without N ₂ O flux	212	73
Chambers with N ₂ O flux	48	139
Of chambers with flux	%	
Quadratic	8	6
Linear	92	94

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261 2.8 Statistical Analysis

262 Statistical analysis was conducted using the PROC GLIMMIX and PROC MIXED
 263 procedures in SAS 9.3 (2002-2010, SAS Institute Inc., Cary, NC, U.S.A.). PROC MIXED
 264 was used to conduct a repeated measures analysis of variance (ANOVA) of the temporal N₂O
 265 and mineral N data. Residual graphs were generated to check for normality. Log
 266 transformation of all temporal data was conducted as there was high variability within the
 267 dataset and nonconformity with the assumptions about normality in ANOVA. Residual
 268 influence statistics were used to identify potential outliers and showed which data points were
 269 the most influential on the entire dataset. These ‘potential outliers’ were then assessed to
 270 check if they were genuine outliers. The assessment of the temporal N₂O data identified only
 271 six individual flux measurements that were ‘genuine outliers’. These were subsequently
 272 removed from the dataset and the average of the other four replicates was then used for that
 273 day for gap-filling to generate the cumulative flux. The PROC GLIMMIX procedure was
 274 used to test for treatment differences in cumulative emissions. Significant differences were
 275 determined according to the F-protected least significant difference test ($p < 0.05$).

Dixons test was used to identify outliers in the ambient data. The minimum detectable flux was then calculated according to Appendix 2 in the chamber methodology guidelines (de Klein and Harvey, 2012). Repeatability, standard deviation and repeatability limit was calculated as per (Ellison et al., 2009). The minimum detectable flux (MDF) was calculated to be 2.59 and 7.78 g N₂O-N ha⁻¹ day⁻¹ in 2013 for small and large chambers, respectively. In 2014 the MDF was calculated to be 2.86 and 7.84 g N₂O-N ha⁻¹ day⁻¹ for small and large chambers, respectively.

3 Results

3.1 Soil and Climatic conditions

The weather during the experiment was typical of the weather for this region with most of the rainfall occurring during the autumn and winter months and the highest temperatures occurring during the summer months (Figure 1a and 2a). In both years, the highest average daily temperature was 17°C in July and the highest total monthly rainfall was in October with 189 mm in 2013 and 173mm in 2014. Total monthly rainfall and average temperature were higher in April (68.4mm) and May (74.8mm) in 2014 compared with April and May 2013 with 47.2mm and 53.6mm and the 30 year average with 59.1 and 55.7mm for April and May respectively. Water filled pore space ranged from 15.74% - 66.09% in 2013 and 28.6% - 68.2% in 2014 with the lowest WFPS% occurring in the summer months. Soil total oxidised nitrogen (TON) and ammonium (NH₄⁺) concentrations increased after fertiliser application (Figure 1b and 2b). Elevated soil TON levels occurred following the 2nd split application of CAN. In 2013, levels reached 95.2 mg TON kg⁻¹ soil two days post-application and 106.8 mg TON kg⁻¹ soil 24 days after application for CAN. After this TON levels from CAN were reduced to below 50 mg TON kg⁻¹ soil. In 2014, TON levels from CAN reached 190 mg TON kg⁻¹ soil three days after application. Generally, all other fertiliser formulations had

lower TON levels than CAN. Urea + DCD and urea + NBPT + DCD levels were similar to the unfertilised control levels. The highest NH_4^+ concentration in 2013 was 161.13 mg NH_4^+ kg^{-1} soil (urea + NBPT + DCD) and in 2014 was 257.98 mg NH_4^+ kg^{-1} soil (urea + DCD). All fertiliser formulations produced an NH_4^+ peak after application but CAN produced the highest TON peak.

3.2 N_2O emissions: fertiliser formulation and N stabilisers at 150 kg N ha^{-1}

Nitrous oxide emissions increased from background levels post-fertiliser application with the highest observed fluxes of 44 g $\text{N}_2\text{O-N ha}^{-1} \text{ d}^{-1}$ in 2013 (Figure 1c) and 43g $\text{N}_2\text{O-N ha}^{-1} \text{ d}^{-1}$ in 2014 (Figure 2c). This peak in N_2O emission corresponded closely with timing of fertiliser application and rainfall occurring 15 and 13 days following the main fertiliser split application in 2013 and 2014 respectively. The association of N_2O emissions with fertiliser application was most pronounced following the second fertiliser application of 120 kg N ha^{-1} . The initial split was 30 kg N ha^{-1} and resulted in a lower quantity of N_2O loss.

In 2013 the largest daily fluxes came from urea, CAN and urea + NBPT, in that order. The profile of temporal emissions from urea + DCD and urea + NBPT + DCD were similar to the unfertilised control. Approximately 16 weeks after fertiliser application, emissions returned to background levels (i.e. similar to that of the unfertilised control) and remained so for the remainder of the year in 2013 for all formulations.

In 2014 there was a peak in emissions after fertiliser application with the largest daily fluxes from CAN, urea + NBPT and urea in that order. Approximately four to six weeks after the second split fertiliser application emissions returned to background levels and remained so for the remainder of the year for all formulations.

3.3 Cumulative emissions and emission factors

Cumulative N₂O emissions were all below 0.5% across all formulations and years. In both years CAN produced significantly higher emissions than the unfertilised control with 1161 g N₂O-N ha⁻¹ in 2013 and 513 g N₂O-N ha⁻¹ in 2014 (Table 4) compared with 424 g N₂O-N ha⁻¹ from the control in 2013 and 191 g N₂O-N ha⁻¹ from the control in 2014. In 2013 N₂O loss from CAN, urea, urea + DCD was not significantly different. Urea + NBPT and urea + NBPT + DCD had significantly lower emissions compared to CAN and were also not significantly different to N₂O emissions from the unfertilised control. In 2014 urea + DCD was the sole fertiliser formulation which had significantly lower N₂O loss compared to CAN, urea and urea + MICO. EFs ranged from 0 – 0.49% with the numerically highest EF of 0.49% from CAN in 2013. CAN and urea had the highest direct EFs in each year and all EFs were lower than the IPCC default of 1% regardless of formulation. Urea + NBPT + DCD had the lowest EF in 2013 and urea + DCD had the lowest EF in 2014 and the lowest mean EF.

351 **Table 4.** Cumulative direct N₂O emissions in g N₂O-N ha⁻¹ and emission factors for 2013 and
 352 2014

Fertiliser Formulation	<u>2013</u>		<u>2014</u>		<u>Average</u>
	Cumulative	Emission	Cumulative	Emission	Emission
	Emissions	Factor	Emissions	Factor	Factor
	g N ₂ O-N ha ⁻¹	(%)	g N ₂ O-N ha ⁻¹	(%)	(%)
CAN	1161a (166)	0.49	513a (94)	0.21	0.35
Urea	889ab (45)	0.31	538a (99)	0.23	0.27
Urea + NBPT	772bc (173)	0.23	427ab (41)	0.16	0.20
Urea + DCD	804ab (140)	0.25	191b (62)	0	0.13
Urea + NBPT + DCD	723bc (105)	0.20	364ab (105)	0.12	0.16
Urea + MICO	N/A N/A		455a (176)	0.18	0.18
Control	423c (57)		191b (95)		

353 *Different letters represent significant differences between treatments for cumulative emissions using F protected LSD test
 354 (P<0.05) and comparisons are within each year

355 *Treatment SE (standard error) for each treatment at each site shown in brackets.

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3.4 Impact of fertiliser rate on N₂O emissions

The impact of N rate (100-200 kg N ha⁻¹) on EF₁ was unclear. There was no significant impact of application rate on the CAN EF in either year as evidenced by the lack of a significant correlation between the EF and N rate (Table 5). However, a significant negative correlation between N rate and the urea EF was observed in 2013 but not in 2014 (Table 5). The model that best fitted this equation was quadratic with an r² value of 0.96; the equation of the line is presented in Table 5.

Table 5. Effect of N rate on N₂O emission factors for CAN and Urea

Treatment	P value (slope different to zero)	Equation *
CAN 2013	0.258	N/A
Urea 2013	0.0321	$y = 8E-05x^2 - 0.0287x + 2.8594$
CAN 2014	0.225	N/A
Urea 2014	0.0811	N/A

*y = Emission factor and x = N fertiliser rate

3.5 N₂O yield efficiency

Nitrous oxide yield efficiency ranged from 0.09 – 0.16 kg N₂O-N t⁻¹ grain in 2013 and 0.02 – 0.07 kg N₂O-N t⁻¹ grain in 2014. There were no significant differences between fertiliser formulations in either year but there were differences between the unfertilised control and fertiliser treatments (Figure 3). In 2013, the unfertilised control was significantly higher than all fertiliser treatments with 0.16 kg N₂O-N t⁻¹ grain except for CAN and in 2014 the unfertilised control was higher than urea + DCD with 0.05 kg N₂O-N t⁻¹ grain and not different to any other treatment.

4 Discussion

4.1 Effect of environmental factors on N_2O emissions

The application of N resulted in a peak in soil mineral N concentrations with CAN producing significantly higher NO_3^- peaks compared to other N forms and all fertiliser formulations producing NH_4^+ peaks. This study showed that using a urea based fertiliser reduced the soil NO_3^- pool compared to CAN. Thus, there is less TON for denitrification and leaching from the urea based fertilisers. The soil NH_4^+ pool was similar regardless of the N formulation used.

Whilst rainfall and temperature at the time of fertiliser application were higher in 2014 than in 2013, cumulative emissions were lower in 2014 compared with 2013. In 2013 there were multiple emission peaks resulting in higher cumulative emissions whereas in 2014 there was one main peak after each fertiliser application. The slightly lower levels of N_2O in 2014 could indicate that either complete denitrification occurred producing N_2 instead of N_2O (Focht et al., 1979), NO_3^- or that the nitrate was leached due to higher rainfall events combined with the free-draining soil texture, or that more N was taken up by the crop due to less drought stress.

In general, cumulative emissions were low ranging from 191 g N_2O-N ha⁻¹ yr⁻¹ to 1161 g N_2O-N ha⁻¹ yr⁻¹ and with EF_1 ranging from 0 to 0.49%. This is consistent with previous studies on spring barley sites in Ireland, where EF for CAN during the growing season (not full year) was observed to be 0.5% (Abdalla et al., 2010). The relatively low EF_1 could be explained, in part, by the soil characteristics. The soil was a free-draining cambisol with a C content of 2.88%, which is typical of Irish arable soils. In a meta-analysis of over 1000 studies, Stehfest and Bouwman (2006) concluded that N_2O emissions were significantly lower on soils with SOC <3% and Gilsanz et al (2016) observed the lowest EFs in soil textures with low clay content (less than 50%) and with sand content greater than 50%. In a

study at three arable sites, the EF₁ for ammonium nitrate was observed to be substantially lower than the default value (0.2% and 0.33%) at two free-draining sites (Bell et al., 2015). In contrast, grasslands exhibit both higher mean emissions and a larger range in EFs (Harty et al., 2016). Dobbie and Smith (2003a) reported EF₁ ranging from 1%-3% in Scottish grasslands whilst previous studies on total N₂O losses in Irish grasslands (including N deposition from fertiliser (EF₁) and animal excreta (EF₃)) have exhibited a range from 0.7% to 7.7% (Hyde et al., 2006; Rafique et al., 2011; Li et al., 2011, Burchill et al., 2014).

4.2 Effect of fertiliser formulation and incorporation of N stabilisers on N₂O emissions

N₂O emission peaks in general corresponded with rainfall events and elevated soil TON and NH₄⁺ concentrations. The majority of N₂O emissions occurred after the second and the larger split fertiliser application with the highest N₂O emissions and EFs associated with CAN and urea application. There were no significant differences in N₂O emissions between CAN and urea. A comparison between urea and ammonium nitrate (AN) at three UK sites also found no differences in N₂O emissions between fertiliser formulations, with higher emissions for both fertilisers at the site with highest rainfall (Bell et al., 2015). Similarly, Louro et al. (2015) reported no significant fertiliser formulation effect on N₂O emissions. In contrast, Dobbie and Smith (2003a) observed lower N₂O emissions associated with urea application compared to ammonium nitrate (AN). This effect was season dependant with no differences when fertiliser was applied in late summer. The findings from this study suggest that the addition of the nitrification inhibitor DCD to urea has potential to reduce N₂O emissions by 30% compared to CAN. The inhibitory effect of DCD can vary depending on climate and soil conditions as well as vegetation type (Gilsanz et al., 2016) and is likely to be more effective where there are higher losses such as wetter soils. Bell et al. (2015) observed a decrease in the EF₁ for AN from 0.55% to 0.06% upon application of DCD. In addition, Dobbie and

Smith (2003a) observed a 50% reduction in cumulative emissions using urea + DCD compared to urea alone, but observed no benefit of urea + NBPT on direct N₂O emissions. The potential effects of DCD uptake by the plant and contamination in crop off takes is needed as recently highlighted in New Zealand (Pal et al., 2016). In studies with higher emissions the inclusion of a urease inhibitor with urea reduced N₂O emissions compared with CAN (McTaggart et al., 1997). While NBPT treated urea did not reduce direct N₂O emissions compared to urea in this study, inclusion of NBPT with urea has been shown to reduce volatilisation from urea (Watson et al., 2009; Forrester et al., 2015) which will reduce indirect N₂O emission associated with the deposition of atmospheric NH₃ (Asman et al., 1998). Urea + MICO showed no effect on N₂O emissions compared to CAN or urea. This corresponds with the literature which shows that urea + MICO is not an effective nitrification or urease inhibitor (Chien et al., 2014; Franzen et al., 2011., Goos, 2013). The EFs for all fertiliser formulations were <50% of the IPCC default value of 1%. Against this background these fertiliser formulations appear to have similar N₂O loss potential in spring barley which tends to be cropped to free draining sites similar to this study. Other studies on arable land in similar climates have also shown EFs lower than the IPCC default (Bell et al., 2015; Abdalla et al., 2010).

The N₂O yield efficiency was highest for the unfertilised control but there were no differences between fertiliser formulations which is in agreement with Hinton et al (2015). It's important to account for crop yield as well as N₂O emissions when assessing fertiliser formulations to determine if they are economically viable (Hinton et al., 2015). This study showed similar N₂O yield efficiency regardless of the fertiliser formulation used.

4.3 Effect of N rate on N₂O emissions

There was no EF response to rate of N application for CAN and urea in 2014. Bell et al (2015) also observed no consistent increase in EF₁ in response to increased rate of AN applied to arable cropped soils. In the current study there was a negative correlation observed between EF₁ and rate of urea application 2014, with EF₁ 0.7% at the lowest N application (100 kg N ha⁻¹) compared to 0.4% at the highest N application (200 kg N ha⁻¹). This may be related to higher ammonia volatilisation occurring at higher N fertiliser application rates (Black et al., 1985; Van der Weerden and Jarvis, 1997). The negative or lack of correlation between EF₁ and applied N rate in the present study indicates that higher NH₃ loss may have taken place and this could result in reduced yields which has been observed in previous studies (Conry et al., 1997; Gately, 1994; Devine and Holmes, 1963). The addition of NBPT protects against this NH₃ loss with reductions of 78.5% on average measured in Irish grassland (Forrestal et al., 2015).

4.5 Emission Factors and comparison to IPCC default

Over the two year period of the study the EFs from all fertiliser formulations ranged from 0% (from urea + DCD in 2014) - 0.49% (from CAN in 2013). Other studies on UK soils have shown higher EFs from AN than those observed from CAN in this study (Hinton et al., 2015; Dobbie et al., 1999). The fact that the highest EF recorded (0.49%) was half the magnitude of the IPCC 1% default, highlights the potential importance of countries moving to a tier 2 methodology using system specific data to generate more accurate N₂O emission inventories. Further research is required in order to determine the appropriateness of the use of the default EF in other scenarios such as different land use types. Furthermore the use of nitrification inhibitors significantly decreased the observed EF. While the use of urease inhibitors did not lead to significant reductions in direct N₂O EFs, potential reductions in ammonia

volatilisation as a result of urease inhibition could significantly reduce indirect N₂O losses associated with the redeposition of atmospheric ammonia (EF₄).

5 Conclusions

Overall, N₂O emissions from the fertilisers tested in this study were less than half the IPCC default value of 1%. The lack of a clear relationship between fertiliser rate and direct N₂O emissions questions the appropriateness of the IPCC default values on soils with low emissions in temperate conditions. This site is representative of the soil type for the majority of spring barley in Ireland and so, based on this study, it is likely that N₂O emissions from the majority of spring barley in Ireland are below the IPCC default value. In terms of fertiliser form, it is important to account for indirect emissions from NH₃ volatilisation when calculating EFs upon switching from ammonium nitrate to urea-based fertiliser forms, as otherwise total emissions associated with N application will be underestimated. The present research emphasises the importance of developing country and system specific emission factors to better estimate greenhouse gas emissions from agriculture.

6 Acknowledgements

We thank the Department of Agriculture, Food and the Marine (Grant No. 11/S/138), the Agricultural Greenhouse Gas Research Initiative for Ireland (Grant No. 10/RD/SC/716) and the Walsh Fellowship Scheme for funding this work. We thank the technical and farm staff at Teagasc Johnstown Castle and Oak Park for their help with sampling and analysis and thanks to Jim Grant for help with statistical analysis. We thank the agricultural catchments program for weather data and farmer James Masterson for access to the field site.

Figure 1. 2013 temporal emissions data (a) daily total rainfall (mm) and daily average temperature (°C) and, (b) daily soil mineral N concentrations (0–10 cm). (c) daily N₂O emissions in g N₂O-N ha⁻¹ day⁻¹ *arrows represent fertiliser application

Figure 2. temporal emissions data (a) daily total rainfall (mm) and daily average temperature (°C) and, (b) daily soil mineral N concentrations (0–10 cm). (c) daily N₂O emissions in g N₂O-N ha⁻¹ day⁻¹ *arrows represent fertiliser application

Figure 3. N₂O yield efficiency (kg N₂O-N t⁻¹ grain) for 2013 and 2014 *Different letters represent significant differences between treatments using F protected LSD test (P<0.05) and comparisons are within each year

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